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The hydration of Portland and aluminous cements with added polymer dispersions

K. M. ATKINS, R. N. EDMONDS, A. J. MAJUMDAR
Building Research Establishment, Garston, Watford, WD2 7JR, UK

We have studied the hydration of ordinary Portland cement and "Secar 71" aluminous cement with added polyvinyl alcohol, polyvinyl acetate, acrylic, poly (vinylidene chloride–acrylic), poly (styrene–acrylic) polymers and poly (styrene–butadiene) rubber latex. We have used the techniques of conduction and differential scanning calorimetry, infrared spectroscopy and X-ray diffraction in our studies.

The nature of the interactions between the polymers and the two cements is significantly different. For Portland cement all polymers were found to retard the hydration rate to some extent, with the acrylics producing the maximum affect, whereas in the case of Secar 71, polymer additions had minimal effects on the hydration of or heat evolution from the cement. Our results suggest that many polymers interact with Portland cements in a chemical way although for aluminous cements the observations are less clear except in the case of polyvinyl alcohol–acetate.

1. Introduction

The study of polymer-modified cements is important for a variety of reasons. Polymer admixtures are known to modify the physical properties of cement pastes [1] and this often leads to improvement in durability. The improved bond strength of polymer cement mortars to concrete substrates is a further advantage, and useful in repair work. Recently it has been shown that water soluble polymers such as polyvinyl alcohol (acetate), when added to aluminous cements, may produce a so-called macrodefect-free (MDF) material of superior strength and fracture toughness [2].

In a previous paper we have reported our findings on the hydration chemistry of an aluminous cement with added polyvinyl alcohol or acetate [3]. We have extended our studies to include Portland cement and other polymers. Many polymers behave differently to the two different cement types and although the effects leading to improvements in the performance of polymer cements are considered to be of a physical rather than a chemical nature we find evidence for chemical reactions in several cases.

2. Experimental procedures

2.1. Materials

"Secar 71" aluminous cement manufactured by Lafarge Aluminous Cement Company was used in this study[†]. As measured by quantitative X-ray diffraction it consisted of 38% CA_2, ~ 50% CA and 1% $C_{12}A_7$*. The ordinary Portlant cement (OPC) used was found to contain 40% C_3S together with C_2S, C_3A and C_4AF as other major phases, all presumably as solid solutions.

The effects of six polymers on the hydration of these two cements were studied by the techniques described below. The polymers were as follows.

(i) Polyvinyl alcohol (PVAl), supplied as a dry powder by Nippon Gohsei. It had been manufactured by almost complete (99 to 100%) hydrolysis of a polyvinyl acetate.

(ii) Polyvinyl acetate (PVAc), also supplied by Nippon Gohsei as a powder. This was a partially (~ 80%) hydrolysed polyvinyl acetate.

(iii) An acrylic ester supplied by Vinyl Products as an aqueous emulsion (~ 50% solids).

(iv) A poly (vinylidene chloride–acrylic ester), copolymer (PVDC) comprising 50% of each monomer by mass, supplied by Scott Bader as an aqueous emulsion (~ 50% solids).

(v) A poly (styrene–acrylic ester), copolymer (AWS) supplied as an aqueous emulsion (~ 50% solids) by BASF.

(vi) A poly (styrene–butadiene) rubber, (SBR) supplied as an aqueous emulsion (~ 50% solids) by Revertex Ltd.

All the emulsions employed some form of detergent as a stabilizer.

2.2. Techniques

The hydration of cements was followed by conduction calorimetry, X-ray diffraction, infrared spectroscopy and differential scanning calorimetry. Some samples

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[†] Some results in the Paper J. Mat. Sci. 24 (1989) pp. 3813–3818 need to be amended in accordance with the new analysis of Secar 71 given here.
*Cement chemistry notation C = CaO, A = Al_2O_3, S = SiO_2 and F = Fe_2O_3.

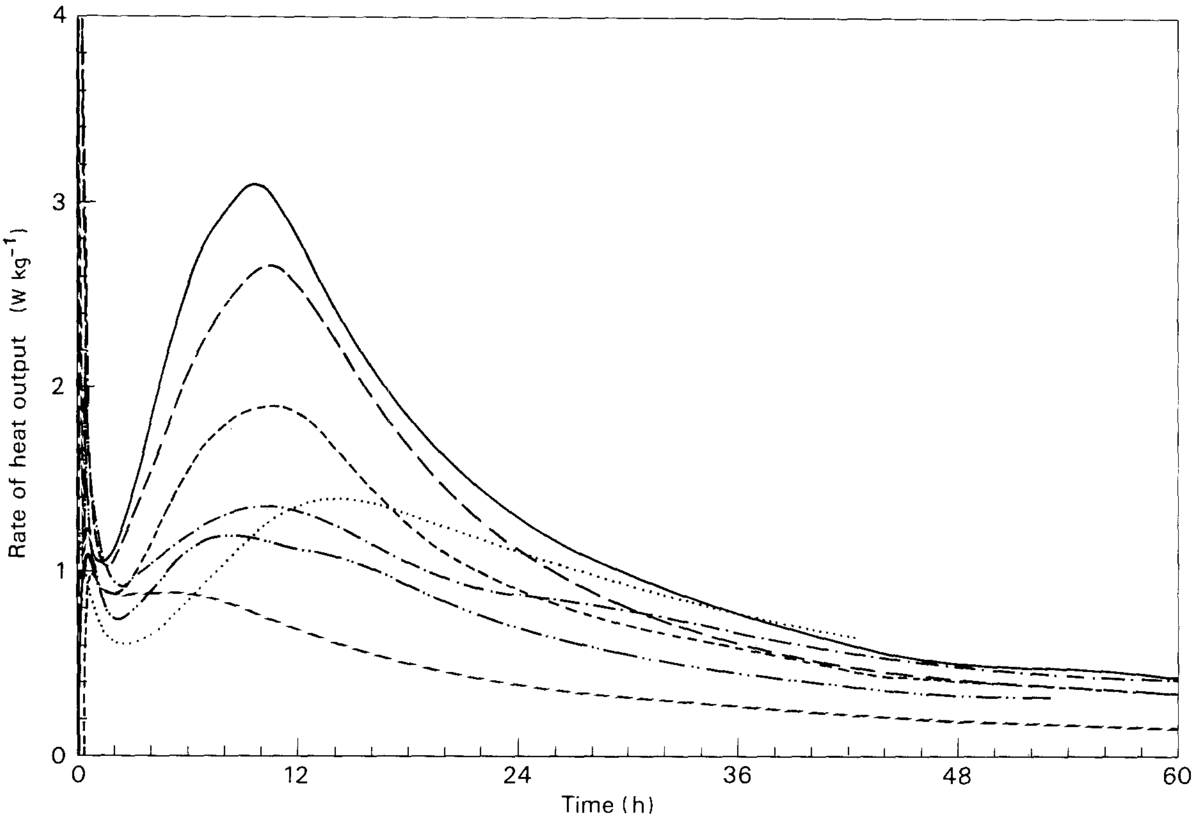

Figure 1 Heat output during hydration of OPC–polymer samples at 20 °C. (——OPC, – – – PVAl, - - - - - SBR, —·—·— PVAc, —··—··— AWS, ······· PVDC, — — — Acrylic)

were examined by scanning electron microscopy and electron probe microanalysis.

For conduction calorimetry experiments, carried out in a Wexham Development JAF calorimeter at 20 °C, a mixture of 10 g of cement and 1 g of polymer with 5 ml of decarbonated distilled water was sealed under nitrogen. Powdered polymers were premixed with dry cement in a shaking apparatus. The emulsified polymers were added together with the water at the start of the experiment. Heat outputs due to cement hydration were continuously monitored, for up to 48 h in the case of "Secar 71" and for up to 72 h for OPC samples. Data were collected and processed on a microcomputer using our own programmes.

The samples for quantitative X-ray analysis were prepared in a similar way except that the OPC–PVAl and OPC–PVAc samples were made using the proportions 10 + 1 + 5 cement + polymer + water whilst the remaining OPC samples had the ratio 8.5 + 1.5 + 3. X-ray measurements were made on a Siemens 0500 diffractometer using copper Kα radiation at 40 kV. For aluminous cement samples the experimental procedures were as described previously [4]. For the OPC samples quantitative X-ray diffraction analysis (QXDA) was used to estimate $Ca(OH)_2$ from its $d = 0.490$ nm peak and C_3S from its $d = 0.302$ nm peak using the $d = 0.348$ nm peak of corundum ($\alpha - Al_2O_3$) as the internal standard. To prepare the samples for X-ray analysis they were micronized using methylated spirit. Earlier work using acetone had shown that some of the polymers dissolved in the acetone causing problems when preparing X-ray samples.

Infrared spectra were recorded on a Grubb–Parsons double beam spectrometer. Powdered samples were mixed with KBr and compressed into discs for analysis. The emulsions were dried in air at 40 °C and the resultant solid was stretched into a film which was thin enough for a spectrum to be taken. A hot air blower usually had to be used to soften the plastic sufficiently for it to be stretched into a film. For further investigation of the acrylic sample, solid $Ca(OH)_2$ was added to the acrylic emulsion. This was then shaken vigorously for a few seconds and then poured into an evaporating basin. The resulting liquid was dried at 40 °C and then stretched as for normal polymer emulsions. A spectrum was taken between 4000 and 400 cm^{-1} wavenumbers.

Differential scanning calorimetry (DSC) analyses were carried out between 20 and 500 °C on a Dupont instrument using alumina as the standard. For electron probe microanalysis (EPMA) samples were taken from 10 mm cubes made from polymer cement pastes and hydrated in a closed atmosphere at 20 °C for two weeks. The specimens for examination under a Cambridge Microscan 9 electron probe were prepared in the usual way [5]. Spot analyses were made of calcium, aluminium, silicon and iron. An "Ovonyx" multilayer crystal enabled measurement be made directly also for carbon and oxygen.

3. Results and discussion

3.1. Conduction calorimetry

The conduction calorimeter traces obtained for various polymer-modified OPC samples up to the first

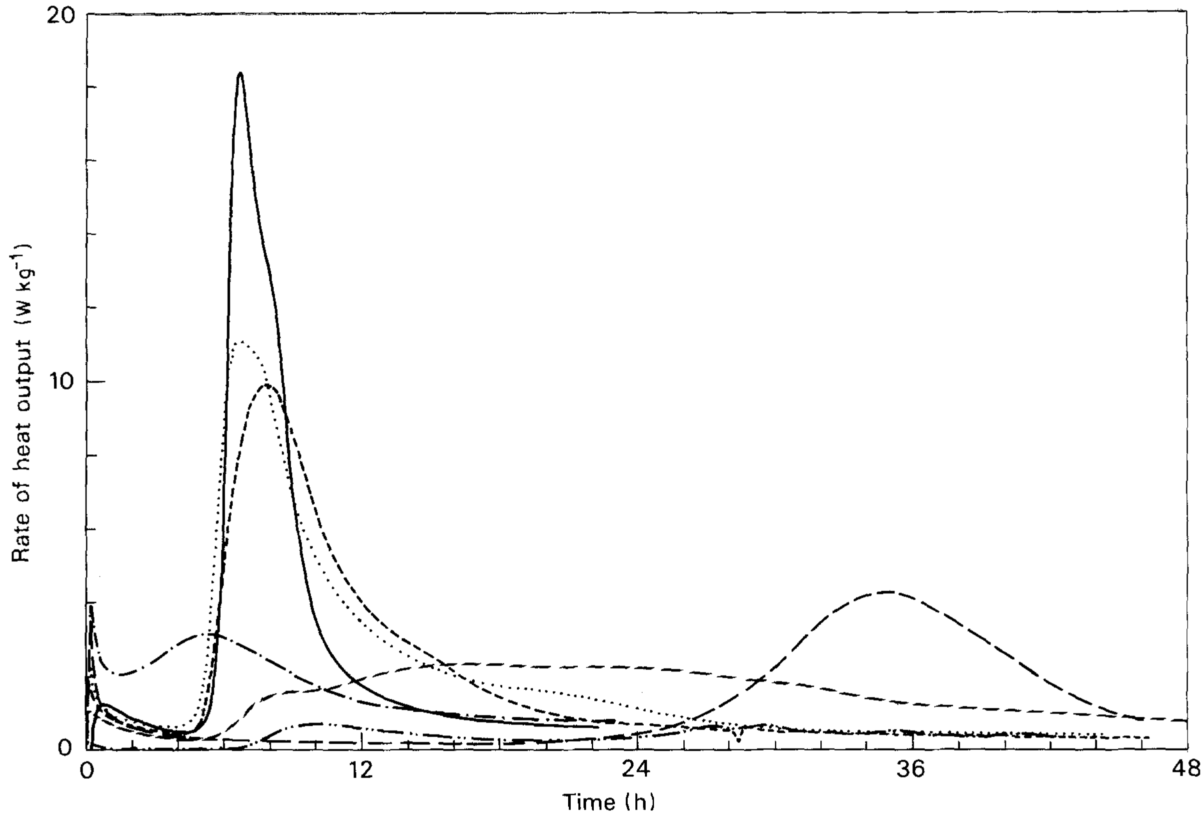

Figure 2 Heat output during hydration of Secar–polymer samples at 20 °C. (—— secar, — — — PVAl, - - - - SBR, —·—·— PVAc, —··—··— AWS, ········ PVDC, — — — acrylic)

60 h of hydration are reproduced in Fig. 1 together with the trace from neat OPC. The broad peak occurring between 2 and 24 h relates to hydration of major cement constituents. For our samples, which had a w/c ratio of 0.5, we obtained a total heat output of 248 kJ kg^{-1} for neat OPC up to 48 h and the maximum rate of heat output was recorded about 12 h after hydration began. The integral heat output for each of the polymer-modified cements is given in Table I.

It is clear that PVAl has very little effect upon the heat output during the hydration of OPC up to 48 h. The SBR has a greater effect but not as much as the AWS or PVAc polymers. The acrylic polymer has almost entirely removed the peak on the hydration curve although the actual heat output remains significant, so hydration could not have stopped completely. The actual time for the maximum in the heat output rate is not affected significantly by the presence of the polymer.

The effect of the polymers on the hydration of the aluminous cement can be seen in Fig. 2. The total heat output for each of the samples up to 48 h is given in Table I. The total heat output is certainly not reduced by the addition of polymers to "Secar 71" – in fact for one of the samples it is slightly increased. For all the samples, however, containing polymers the heat evolution peak is lower and broader than that of the neat cement. For the sample containing acrylic polymer the peak is very wide and uneven. For the PVAl sample the appearance of the peak is much delayed.

3.2. X-ray analysis

The amounts of the C_3S phase present in OPC pastes containing the different polymers after one week of hydration as determined by QXDA are shown in Table II. The accuracy of the results is perhaps no better than 10% but it is clear that some polymers, for instance acrylics, reduce the rate of hydration of C_3S

TABLE I Heat output (kJ kg^{-1}) during the first 48 h hydration of Portland and aluminous cements with various added polymers

OPC	Polymer	Secar
248	No polymer	308
224	PVAl	249
158	PVAc	204
121	Acrylic	261
128	AWS	—
165	PVDC	321
157	SBR	292

TABLE II Percentage C_3S (by mass) in samples after one week hydration

Sample		C_3S (%)
Unhydrated OPC		40
One week	AWS	16
	PVDC	19
	SBR	21
	Acrylic	27
	Neat OPC	13

TABLE III Composition (% by mass) of Secar 71 after hydration

Sample	Hydration period (h)	CA (%)	CAH_{10} (%)
Neat cement	24	14	24
PVAl	72	15	3
PVAc	72	20	0
Acrylic	72	13	24
PVDC	48	12	36
SBR	48	16	21

and hence of the cement in a significant way, at least during the first week of hydration.

After 48 h of hydration we have obtained the following estimates (by mass) for $Ca(OH)_2$ in the various samples: 5% in neat OPC, 4% in OPC modified by AWS and PVDC and 3% for the SBR modified sample. No $Ca(OH)_2$ was detected in the OPC sample containing acrylic polymer. We believe the accuracy in these measurements to be poor due to some carbonation in some samples and possibly due to preferred orientation of $Ca(OH)_2$ crystals. Nevertheless it appears that acrylic polymers severely hinder the formation of $Ca(OH)_2$ crystals during the early hydration of OPC.

The QXDA results showing the effect of polymer addition on the hydration of Secar 71 are given in Table III. The addition of PVAl and PVAc causes no reduction in the amounts of calcium aluminates consumed although it is known [3] that only a small quantity of crystalline hydrates is produced in these cases. Other polymers had very little effect on the phase composition of the hydrated cement. The X-ray results are broadly in agreement with the findings from conduction calorimetry.

3.3. Infrared spectroscopy

The infrared spectrum of unhydrated OPC (part of which is shown in Fig. 3a) has characteristic absorptions at 3400, 1610, 1430 cm^{-1} and several other wavenumbers below 1200 cm^{-1}. It is likely that the 3400 and 1610 cm^{-1} peaks correspond to stretching and bending modes of water of crystallization (particularly from gypsum) in the solid. The peak at 1430 cm^{-1} is common to neat OPC and all OPC–polymer samples and is likely to be due to some lattice vibration of a calcium silicate structure. After hydration for 48 h the peaks at 3400 and 1610 cm^{-1} are much amplified. The 1610 cm^{-1} peak has shifted to 1635 cm^{-1}, which is probably due to a change in the way the water is actually bound in the lattice. The absorption pattern below 1200 cm^{-1} is only changed slightly.

The spectrum of the PVDC film has bands at 2850 and 2950 cm^{-1} due to the two normal modes of the CH_2 groups of the polymer backbone as well as to all the other CH band stretching vibrations of this polymer. There is also an absorption maximum at 1730 cm^{-1} due to the carbonyl group of the acrylic functionality. An absorption at 1430 cm^{-1} results from an alkane type vibration of the polymer backbone. Absorption maxima below this (in the so-called "fingerprint" region) are difficult to assign and so are of less use diagnostically [6]. One would expect two strong absorption maxima at 600 to 800 cm^{-1} due to the CCl_2 groups but for some reason they are either absent or just too small to register.

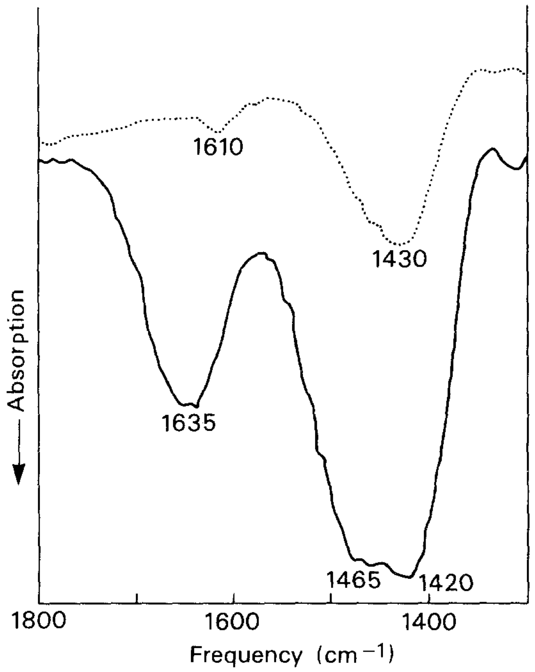

Figure 3 Part of the infrared spectra of unhydrated (········) and hydrated (———) OPC.

Fig. 4a shows part of the spectrum of a 2 week hydrated PVDC–OPC sample. All the peaks present in the PVDC film are present, which implies that the polymer has not been drastically altered. By comparing Fig. 4a with Fig. 3b, it is clear that the hydration of the cement has not been prevented – the water peak at 1630 cm^{-1} has developed fully. IR has not been developed as a quantitative tool, thus the degree of hydration cannot be measured using IR.

The acrylic–styrene copolymer IR spectrum had maxima at 2800 to 3000 cm^{-1} (C–H stretches), 1715 cm^{-1} (the acrylic ester carbonyl stretch) 1600 cm^{-1}, 1580 cm^{-1} and 1500 cm^{-1} (all three are characteristic of a phenyl group [6]). The peak at 1715 cm^{-1} which is a very strong one has a shoulder at 1730 cm^{-1}. In the fingerprint region peaks at 690 and 750 cm^{-1} are likely to be out of plane bending of the monosubstituted phenyl ring of the polymer.

In the IR spectrum of the cement modified by acrylic–styrene copolymer the carbonyl peak has shifted to 1725 cm^{-1} and lost its shoulder. Apart from the C–H stretching at 2900 cm^{-1} no other polymer peaks are strong enough to be observed in the cement. All the peaks present in the hydrated cement sample are present.

The IR spectrum of the SBR sample has C–H stretches at 2800 to 3000 cm^{-1} and the phenyl absorptions at 1500 to 1600 cm^{-1}. At 1630 cm^{-1} the C=C vibration of the polymer backbone is visible. The introduction of the SBR polymer into a cement paste

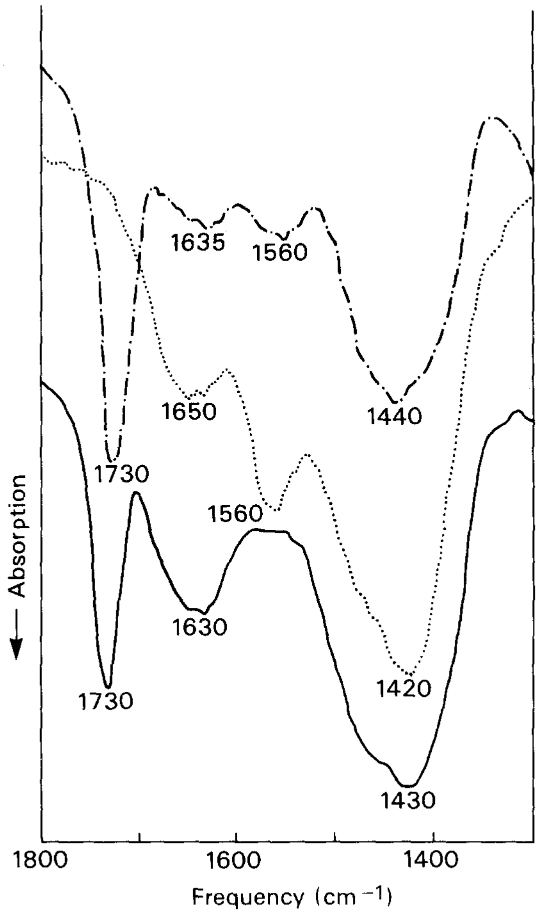

Figure 4 Part of the infrared spectra of hydrated polymer–OPC materials PVDC sample hydrated for two weeks (——), PVAc sample hydrated for two days (·····), polyacrylic sample hydrated for two weeks (—·—·—).

does not really affect the IR spectrum of the paste except that at 2900 cm^{-1} we see the C–H stretching absorption.

The spectrum of PVAl shows a small peak at 1710 cm^{-1} which implies that the hydrolysis of the polymer is not complete. (The manufacturer only claims 99% hydrolysis!) The PVAl has no significant effect upon the IR spectrum of the hydrated cement paste.

The spectrum of PVAc shows a larger carbonyl group absorption than in PVAl, as would be expected since this polymer has been hydrolysed less. However a strong OH peak is also present at 3400 cm^{-1} because the material is substantially hydrolysed. In the OPC–PVAc sample that was hydrolysed for 48 h (Fig. 4b) no carbonyl peak is present indicating that hydrolysis has been completed. There is however, a new peak at 1560 cm^{-1} which corresponds to a carboxylate group. This is the asymmetrical vibration, the symmetrical vibration expected at 1300 to 1420 cm^{-1} [6] is obscured by the cement peak. It appears, therefore, that the ester linkage has been broken to form polyvinyl alcohol and an acetate ion CH_3COO^-. No evidence for crystalline calcium acetate is seen in the X-ray diagrams of these samples.

A part of the spectrum of this polyacrylic film is shown in Fig. 5a. There is a very distinct carbonyl absorption at 1720 cm^{-1} with a shoulder at 1740 cm^{-1}.

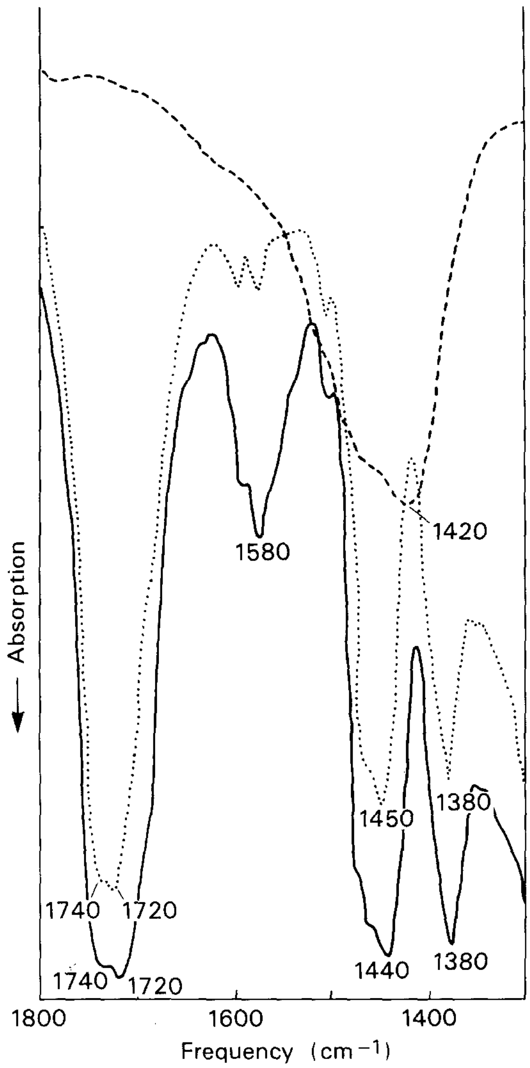

Figure 5 Part of the infrared spectra of polymer films and calcium hydroxide Polyacrylic film (·····), polyacrylic film with $Ca(OH)_2$ added to emulsion before drying (——), calcium hydroxide (– – – –).

Alkane type peaks occur at 1440 and 1330 cm^{-1}. The smaller peaks at 1500 to 1600 cm^{-1} are probably due to a phenyl group present in the surfactant or some other impurity. On adding this polymer to OPC and hydrating we get a trace as in Fig. 4c. The carboxyl peak is still present but apparently some hydrolysis has occurred as the antisymmetric carboxylate stretch is seen at 1580 cm^{-1}. The water bend at 1635 cm^{-1} has been inhibited so we only have a small peak at this frequency. The carboxylate peak was found to get larger as hydration progressed – though no detailed quantitative work has been done.

Further investigative work was carried out with the acrylic sample. Upon addition of $Ca(OH)_2$ to the emulsion, a film was produced which gave a spectrum, part of which is shown (Fig. 5b). A peak at 1580 cm^{-1} is likely to be a carboxylate antisymmetric stretch. (As a check a spectrum of pure calcium hydroxide was taken (Fig. 5c).) This had a peak at 1420 cm^{-1} and none around 1580 cm^{-1}. This implies that the ester linkage of the acrylic group is broken leaving a negatively charged carboxylate group. This will probably complex a calcium ion. The difference in 20 cm^{-1}

between the position of the carboxylate group in the film and in the cement could well be due to the differences in the bonding to carbon. The slow hydrolysis of acrylics has been previously observed, both with acrylic esters [7] and with polyacrylamide [8].

The above observations suggest that the AWS polymer can probably be treated as a "dilute acrylic", in that the styrene groups will probably have little effect upon the hydration of cement.

The PVDC polymer also has acrylic groups separated by another monomer. It is probably fair to assume that the CCl_2 groups do not greatly affect the hydration of the cement but once they are dehalogenated to carbonyl groups they could have a much larger effect. The effect of the released Cl^- ions must also be considered. Less work was carried out upon the Secar–polymer samples by infrared spectroscopy, however, some results did become clear. The acrylic ester was not hydrolysed by the alumina cement (no carboxylate peak appeared in the IR spectrum); it appears that in order for hydrolysis to occur, the high pHs found in the OPC samples is required, however, the PVAc polymer is hydrolysed by the aluminous cement.

3.4. Differential scanning calorimetry (DSC)

DSC measurements on OPC–polymer mixes showed endotherms due to the loss of absorbed water at about 80 °C and to the dehydration of calcium hydroxide at 450 °C. Between these two was an exotherm due to oxidation of polymer. PVAc and PVAl gave a low broad exotherm at around 300 °C; polyacrylic gave a sharper signal at 380 °C. PVDC gave two signals at 260 and 320 °C. As hydration increased in the PVDC samples, the balance between the two signals changed. After 48 h hydration the two peaks are of equal height (though the 320 °C peak is broader). At 7 days the 320 °C peak is higher than the 260 °C peak. As time progressed, the 320 °C peak became higher and the 260 °C peak diminished. It has been reported [9] that a pure poly (vinylidlene chloride) polymer undergoes dehalogenation in the highly alkaline cement medium and so produces a carbonyl group. It is possible that in our vinylidene chloride–acrylic copolymer we also see dehalogenation, the 260 °C peak resulting from undehalogenated polymer and the 320 °C peak resulting from the oxidation of dehalogenated polymer which increases in concentration with time. It is more likely that the carbonyl groups interact with calcium ions rather than the chlorine atoms so that the dehalogenated polymer is more stable, hence it will oxidize at a higher temperature.

DSC analyses of Secar–polymer samples showed signals corresponding to CAH_{10}, AH_3 and polymer as expected.

3.5. Electron probe microanalysis

EPMA measurements on polymer modified OPC samples showed no significant differences from pure OPC samples, except that the carbon content of the hydrated region was significantly higher than in the visible C_3S grains. This is due to the polymer being dispersed in the hydrated region and failing to penetrate the grains themselves. Individual polymer particles were not visible but as the expected size of the polymer particles ($\sim 1\ \mu m$) is less than the resolution of the EPMA this is not conclusive proof that the polymers have been chemically absorbed into the hydrated phase.

In Secar–PVAl and Secar–PVAc samples calcium rich hydration shells have been reported [3]. However no such shells were seen in any of the Secar samples modified by other polymers. Again the only difference between Secar samples with the other polymers present and the control samples is the higher carbon concentration in the hydrated region.

Our observations on the nature of polymer modified cements tend to indicate rather strongly that in some cases, for instance OPC–acrylics, there is chemical interaction between the two components. The acrylic polymer is partially hydrolysed by alkaline OPC and the resulting carboxylate ions may "complex" the calcium ions of the unhydrated cement. As a result it is difficult for water to reach the cement grain and the overall effect is a reduction in the rate of hydration of and heat evolution from the cement. The PVDC–acrylic and styrene–acrylic polymers behave like acrylic but as they have fewer acrylic units per mass of the polymer, the effect is not as pronounced as with the latter.

4. Conclusions

Polymer dispersions interact differently with Portland and aluminous cements. Of the six polymers studied all except PVAl retard the hydration of OPC to some extent. SBR and PVAl appear to have very little *chemical* interaction with OPC while PVAc is fully hydrolysed. Acrylic based polymers are partially hydrolysed in the OPC environment and have a marked effect on the rate of cement hydration. The dehalogenation of PVDC may not be important in this context.

With "Secar 71" aluminous cement only PVAl–PVAc has given interesting results [3]. The other polymers studied showed very little effect on the rate of hydration of the cement and the hydration shells seen in the PVAl–PVAc modified Secar 71 were not observed in pastes containing the other polymers. PVAc was partially hydrolysed in the alkaline cement environment.

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